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(54) Title: MEASURING CHLORINE CONCENTRATION

(57) Abstract

The concentration of a dissolved chlorine-containing species is monitored using an amperometric cell having a platinum working electrode, a counter electrode and a reference electrode. Water the chlorine concentration of which is to be monitored is tested to determine the current (i_1) through the cell associated with the dischargeable chlorine-containing species, and the pH (pH1) of the water. The values of i_1, pH1 and a calibration factor, μ (representative of the current generated in the cell per unit concentration of the said electrochemically dischargeable species), are used to calculate the total concentration (Cl_{tot}) of dissolved chlorine as a function of the fraction (f_1) (formula (10) where x is 2.50 to 7.53 and y is 3.00 to 5.00.

$$f_1 = \frac{1}{1 + \frac{10^{-x}}{y^{-pH1}}} \quad (10)$$

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MEASURING CHLORINE CONCENTRATION

The present invention relates to a method of measuring the concentration of residual chlorine in water.

Water from reservoirs is generally treated with a disinfecting agent before being supplied to the public as drinking water. The disinfecting agent serves to control or kill bacteria present in the reservoir water and therefore render it safe for human consumption.

One commonly used disinfecting agent is chlorine which may be added to the water as elemental chlorine or sodium hypochlorite. The treated water contains an amount of residual chlorine which should be between predetermined upper and lower limits, the former (i.e. upper limit) being to ensure that the water is safe for consumption and the latter (i.e. lower limit) being to ensure that the chlorine is present in an amount sufficient to provide effective bacteriostatic or bacteriocidal control.

Thus, tests on the treated water are carried out to ensure that the chlorine is within the predetermined limits. If not, then the amount of sodium hypochlorite or elemental chlorine added to the water may be adjusted accordingly to ensure that the residual chlorine content of the treated water is between said limits.

The residual chlorine is considered to be present as HOCl and OCl⁻ which co-exist in accordance with the equation (1)

$$HOCl \longrightarrow OCl^- + H^+ \qquad (1)$$
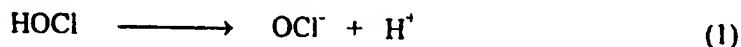
Numerous methods for measuring the total residual chlorine content of water are known. One such method utilises an amperometric cell which comprises a platinum working electrode, a counter electrode (e.g. platinum), and a reference electrode (e.g. silver/silver chloride). An example of such a cell is the DEPOLOX 4 as manufactured by Wallace & Tiernan Limited.

Such amperometric cells make use of the fact that

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1.   The HOCl component of the residual chlorine may be discharged at the
      working electrode of the cell in accordance with the equation (2)

$$HOCl \ + \ 2\varepsilon \ \longrightarrow \ OH^- \ + \ Cl^- \qquad (2)$$

2.   This discharge provides a current, i, which is proportional to the concentration
      (Cl_{HOCl}) of chlorine present as HOCl in the water. Thus

$$Cl_{HOCl} = \frac{i}{\mu} \qquad (3)$$

      where μ is a calibration factor representative of the current generated in the
      cell per unit amount of HOCl.

      In practice, the water to be monitored by the cell is buffered to a pH of about
6. This ensures that the equilibrium of equation 1 is shifted almost wholly to the left
so that substantially all residual chlorine is present as HOCl, i.e. the electrochemically
dischargeable species.   The current measured by the cell is therefore directly
representative of the total amount (Cl_{tot}) of dissolved chlorine in the buffered water.

      There are however two disadvantages with this method of operation.

      Firstly, the need to add a buffer to the water represents a significant extra cost
to the measurement operation both in terms of the cost of the buffering chemicals and
the cost of disposing of the buffered water, of which large quantities are generated.

      Secondly, the measurement provides no information on the relative amount of
HOCl and OCl⁻ in the unbuffered sample. This information may be required as HOCl
is considered to be the main disinfecting species and therefore its actual concentration
in the unbuffered water may be of importance. To obtain this information it is
necessary to make a separate measurement of the pH of the unbuffered water and then
to calculate the actual amount of HOCl (in the unbuffered sample) on the basis of the
following.

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For a given pH, the concentration of HOCl in the water is a particular fraction, f, of the total amount of dissolved chlorine (some of which is provided by the OCl⁻ species - see equation (1) above), i.e.

$$Cl_{HOCl} = f.Cl_{tot} \qquad (4)$$

The fraction f for a particular pH may be determined in accordance with equation (3):

$$f = \frac{1}{1 + \dfrac{10^{-Ka}}{10^{-pH}}} \qquad (5)$$

where pH is the pH of the unbuffered water and Ka is the dissociation constant at the temperature T°C of measurement as given by equation (6)

$$K_a = \left(\frac{3000}{T+273} - 10.0686\right) + \left[0.0253.(T+273)\right] \qquad (6)$$

Typically Ka is about 7.53 for a pH of 7 and a temperature of 25°C.

The concentration of HOCl (Cl_{HOCl}) in the unbuffered water may then be determined from equation (4)

Therefore in order to obtain the value of Cl_{HOCl} (in the unbuffered water) it is necessary (in accordance with conventional practice) to make separate measurements on buffered and unbuffered samples of the water and then to obtain the value of Cl_{HOCl} as described above.

It would in theory be possible to make the measurement in the amperometric cell using unbuffered water and then to calculate the values of Cl_{tot} and Cl_{HOCl} using the following equations

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$$Cl_{HOCl} = \frac{i}{\mu} \tag{3}$$

$$Cl_{tot} = \frac{Cl_{HOCl}}{f} \tag{4}$$

$$\therefore \quad Cl_{tot} = \frac{i}{\mu} \left(1 + \frac{10^{-Ka}}{10^{-pH}} \right) \tag{7}$$

where pH is the pH of the (unbuffered) water whereof the chlorine concentration is being monitored. However we have established that equation (6) does not provide an accurate value of Cl_{tot} on the entire range of pH values likely to be encountered. More particularly the bracketed expression (which is equivalent to $1/f$) does not accurately define the fraction f at pH values in the range 6 to 8.5 and in fact leads to excessively high values of Cl_{tot}.

It is therefore an object of the present invention to obviate or mitigate the abovementioned disadvantages.

According to the present invention there is provided a method of monitoring the concentration of dissolved chlorine containing species using an amperometric cell having a platinum working electrode, a counter electrode and a reference electrode, the method comprising the steps of

(A)   testing water whereof the chlorine concentration is to be monitored to determine

(a)   the current (i_1) through the cell associated with the discharge, at the working electrode, of electrochemically dischargeable chlorine containing species

(b)   the pH (pH1) of the water, and

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(B)   using the values of i_1, pH1 and a calibration factor, μ, (representative of the current generated in the cell per unit concentration of said electrochemically dischargeable species) to calculate the total concentration (Cll_{tot}) of dissolved chlorine as a function of the fraction (f_1)

$$f_1 = \frac{1}{1 + \dfrac{10^{-x}}{y^{-pH1}}} \qquad\qquad (10)$$

where x is 2.50 to 7.53 and y is 3.00 to 5.00

We have established that (for an amperometric cell having a platinum working electrode, a counter electrode and a reference electrode) equation 10 provides an accurate representation of the fraction, f_1, of the amount of electrochemically dischargeable residual chlorine containing species relative to the total residual chlorine at any pH over a relatively wide pH range, e.g. 6 to 8.5. More particularly, equation 10 provides a much more accurate model than that provided by the conventionally used equation 5. The fraction f_1 may then be used in a determination of the total amount of dissolved chlorine or the amount of dissolved chlorine present as electrochemically dischargeable species.

In accordance with the invention it is possible to make pH and current measurements on unbuffered water samples and use the values and pH1 of i_1 obtained to calculate the concentrations set out in the preceding sentence. The fact that accurate measurements may be made on unbuffered water is a significant advance over the prior art since the expense associated with addition of buffers and disposal of the buffered water are avoided. Furthermore the electrochemical measurement (i.e. using the cell of the kind defined) and the pH measurement may be effected on the same sample of water so that the need for separate measurements on buffered and unbuffered samples is avoided.

The total amount (Cll_{tot}) of dissolved chlorine may be determined in accordance with the equation

$$Cll_{tot} = \frac{i_1}{\mu f}$$

$$= \frac{i_1}{\mu}\left(1 + \frac{10^{-x}}{y^{pH1}}\right) \qquad (11)$$

As an equivalent of this calculation, it is possible separately to calculate

(i)   the value of f_1 (the fraction of HOCl) from equation (1),

(ii)   the amount of dissolved chlorine Cll_{dis} present as said electrochemically dischargeable species in accordance with the equation

$$Cll_{dis} = \frac{i_1}{\mu} \qquad (12)$$

(iii)   the total amount of dissolved chlorine in accordance with equation

$$Cll_{tot} = \frac{Cll_{dis}}{f} \qquad (13)$$

which is the equivalent of

$$Cll_{tot} = \frac{i_1}{\mu}\left(1 + \frac{10^{-x}}{y^{-pH1}}\right) \qquad (11)$$

As a further alternative, it is possible initially to calculate a value $I_{100\%}$ where

$$I_{100\%} = i_1\left(1 + \frac{10^{-x}}{y^{pH1}}\right) \qquad (14)$$

and corresponds to the current which would have been generated in the cell if all of the residual chlorine had been present as electrochemically dischargeable species. The value of Cll_{tot} may then be calculated in accordance with the equation

$$Cll_{tot} = \frac{I_{100\%}}{\mu} \qquad (15)$$

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It will be appreciated that equation (15) is, in effect, equivalent to equation (11).

Equation (10) incorporates the parameters x and y which are such that x is in the range 2.50 to 7.53 and y is in the range 3.00 to 5.00 The particular value of x used in the calculation of equation (10) will also generally be that used for equation (12) and similarly for y will be kept constant for the various calculations.

If the method of the invention is employed at high pH values then the values employed for x and y may be different from those employed at lower pH values, although generally only x will need to be varied.

Preferably x is in the range of 4.5 to 5.1, more preferably 4.7 to 4.9, and most preferably about 4.8. Preferably y is in the range 3.5 to 4.5, more preferably 3.8 to 4.2 and most preferably about 4. We have found values of x = 4.83 and y = 4.00 to be particularly suitable for measurements effected at ambient temperature.

Prior to use in the method of the invention, the cell is calibrated to determine a calibration factor, μ, which represents the current generated in the cell per unit concentration of electrochemically dischargeable species. Generally i_1 is measured in microamps and μ has the units of microamps per ppm of the electrochemically dischargeable species in which case the value of $C11_{dis}$ is obtained in ppm. It will however be appreciated that, if desired, other units may be employed for i, and μ.

Conveniently the cell is calibrated by

(w)   using a sample of water ("calibration water") containing a known total concentration ($C12_{tot}$) of dissolved residual chlorine containing species to measure the current flow (i_2) through the cell associated with the discharge, at the working electrode, of electrochemically dischargeable chlorine containing species,

(x)   measuring the pH (pH2) of the calibration water sample,

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(y)   determining the fraction (f_2) of the total dissolved chlorine which is present as said electrochemically dischargeable species by the equation,

$$f_2 = \frac{1}{1 + \dfrac{10^{-x}}{y^{-pH2}}} \qquad (15)$$

where x is 2.50 to 7.53 and y is 3.00 to 5.00,

(z)   using the values of i_2, f_2 and $Cl2_{tot}$ to determine a calibration factor (μ) for the cell representative of the amount of current per unit concentration of said electrochemically dischargeable species:

The value of μ may for example be calculated in accordance with the following equations

$$Cl2_{dis} = f_2 . Cl2_{tot} \qquad (16)$$

$$\mu = \frac{i_2}{Cl2_{dis}} \qquad (17)$$

Alternatively μ may be calculated from the following equations

$$I_{cal} = i_2 \left(1 + \frac{10^{-x}}{y^{-pH2}} \right) \qquad (17)$$

(where I_{cal} corresponds to the current which would have been generated in the cell if all of the residual chlorine had been present as electrochemically dischargeable species) and

$$\mu = \frac{I_{cal}}{Cl2_{hu}} \tag{18}$$

The "calibration water" may be a water sample which has been "made up" so as to have a known total concentration of residual chlorine. It is however also possible for the "calibration water" to be a sample of the water whereof the chlorine concentration is being measured by the amperometric cell, in which case the "calibration sample" may have its total dissolved chlorine measured by a different technique (e.g. colorimetric analysis).

The values of x and y used in equation 13 will generally be the same as those employed in equation 10.

The method of the invention employs an amperometric cell having a platinum working electrode, a counter electrode and a reference electrode. The working electrode may be maintained at a fixed potential with respect to the reference electrode by means of a feedback "potentiostatic" electronic circuit. Preferably the platinum working electrode is maintained at a potential of 250 mV relative to the reference electrode. Preferably the counter electrode is of platinum.

Preferably the reference electrode is a silver/silver chloride electrode placed in a potassium chloride electrolyte which makes contact with the water to be monitored via a porous junction.

A particularly suitable cell for use in the method of the invention is the DEPOLOX 4 cell as manufactured by Wallace & Tiernan Ltd. Such a cell may be operated on a continuous basis to monitor the amount of dissolved chlorine in water.

It will be appreciated that a microprocessor may be used to convert current readings to concentration values, calibration factors etc.

The invention will be illustrated by reference to the following non-limiting Example which is to be read in conjunction with Figs. 1 and 2 of the accompanying drawings.

<u>Example</u>

The current i_1 generated in a DEPOLOX 4 cell by a solution containing 0.4 ppm total dissolved chlorine (Cl_{tot}) was measured over a range of pH values. The results are plotted in Fig. 1.

The following calculations were then performed to compare the accuracy of results obtained using the method of the invention with those obtained using the prior art calculations. In the following calculations the calibration factor, μ for the cell was obtained using the current value (10.5μA) measured at pH = 7.5.

<u>Invention</u>

From Equation (10) and using x = 4.83 and y = 4.

$$f_1 = \cfrac{1}{1 + \cfrac{10^{-4.83}}{4^{-7.5}}}$$

$$\therefore f_1 = 0.674$$

Therefore (at pH = 7.5) 67.4% of the total dissolved chlorine is calculated to be present as electrochemically dischargeable species (considered to be HOCl).

Hence if all dissolved chlorine had been present as HOCl this would have provided a current I as given by the following equation

$$I = 10.5\left(1 + \frac{10^{-4.87}}{4^{-7.5}}\right)$$

$$\therefore I = 15.589$$

$\therefore$ Calibration factor μ for cell corresponds to 15.589 μA per 0.4 ppm present as HOCl.

$$\therefore \mu = \frac{15.589}{0.4} \text{ } \mu\text{A per ppm HOCl}$$

$$\therefore \mu = 38.973 \text{ } \mu\text{A per ppm HOCl}$$

(μ may alternatively be calculated by the following)

$$\left(\right)$$

$$\left(\mu = \frac{i}{f_1 . Cl_{tot}} \right)$$

Now, for any particular pH, the measured current may be converted to a current $I_{100\%}$ which would have been obtained if all of the dissolved chlorine had been present as HOCl in accordance with the following equation (based on equation (14) above)

$$I_{100\%} = i\left(1 + \frac{10^{4.83}}{4^{-pH}}\right)$$

Moreover

$$Cl_{tot} = \frac{I_{100\%}}{\mu} \tag{15}$$

Using the current i and pH readings plotted in Fig. 1, values of $I_{100\%}$ were obtained for a range of pH values and subsequently the corresponding values of Cl_{tot} were obtained.

The results are plotted in Fig. 2 from which it will be seen that the mathematical model of the invention consistently gives a value of, or very close to, 0.4 ppm (i.e. the actual concentration of the solution).

Comparison

From equation (5) and using Ka = 7.53 at a pH = 7.5.

$$f = \frac{1}{1 + \dfrac{10^{7.53}}{10^{-7.5}}}$$

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$$= 0.517$$

Therefore 51.7% of the total dissolved chlorine is calculated to be present as electrochemically dischargeable species (considered to be HOCl).

Hence if all dissolved chlorine had been present as HOCl this would have provided a current I given by the following equations

$$I = 10.5\left(1 + \frac{10^{-7.53}}{10^{-7.5}}\right)$$

$$= 20.299\ \mu A$$

$$\text{Now } \mu = \frac{I}{Cl_{tot}}$$

$$\therefore \mu = 50.748\ \mu A \text{ per ppm HOCl.}$$

On this comparative model

$$I_{100\%} = i\left(1 + \frac{10^{-7.53}}{10^{-7.5}}\right)$$

As previously, values of $I_{100\%}$ were obtained to provide Cl_{tot} values for a range of pH values. The results are also plotted in Fig. 2.

From a comparison of the two lines in Fig. 2, it will be seen that the comparative model is accurate at a pH of only about 7.5, below which the values of Cl_{tot} are significantly less than 0.4 ppm and above which the values of Cl_{tot} are significantly higher than 0.4ppm. Thus, at pH = 8, the comparative model provides a value of Cl_{tot} of about 0.6 ppm, i.e. 50% greater than the true value. Hence the comparative model can only be used if the water has been buffered to a pH at which the model is accurate.

It will thus be appreciated from Fig. 2 that the method of the invention provides accurate values of Cl_{tot} over a range of pH values thus avoiding the need to buffer the water.

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CLAIMS

1.   A method of monitoring the concentration of dissolved chlorine containing species using an amperometric cell having a platinum working electrode, a counter electrode and a reference electrode, the method comprising the steps of

(A)   testing water whereof the chlorine concentration is to be monitored to determine

(a)   the current (i_1) through the cell associated with the discharge, at the working electrode, of electrochemically dischargeable chlorine containing species

(b)   the pH (pH1) of the water, and

(B)   using the values of i_1, pH1 and a calibration factor, μ, (representative of the current generated in the cell per unit concentration of said electrochemically dischargeable species) to calculate the total concentration (Cll_{tot}) of dissolved chlorine as a function the fraction (f_1)

$$f_1 = \frac{1}{1 + \dfrac{10^{-x}}{y^{-pH1}}} \qquad (10)$$

where x is 2.50 to 7.53 and y is 3.00 to 5.00

2.   A method as claimed in claim 1 wherein Cll_{tot} is calculated in accordance with
the equation

$$Cll_{tot} = \frac{i_t}{\mu}\left[1 + \frac{10^{-x}}{10^{-pHl}}\right] \qquad (11)$$

where x and y are as defined in claim 1

2.   A method as claimed in claim 1 or 2 wherein x is in the range 4.5 to 5.1.

4.   A method as claimed in claim 3 wherein x is in the range 4.7 to 4.9.

5.   A method as claimed in claim 1 or 2 wherein x is about 4.8.

6.   A method as claimed in any one of claims 1 to 5 wherein y is in the range 3.5
to 4.5.

7.   A method as claimed in claim 6 wherein y is in the range 3.8 to 4.2.

8.   A method as claimed in claim 7 wherein y is about 4.00.

9.   A method as claimed in claim 1 or 2 wherein x is 4.83 and y = 4.00.

10.   A method as claimed in any one of claims 1 to 8 wherein the value of μ is
obtained by

        (w)   using a sample of water ("calibration water") containing a known total
        concentration ($C12_{tot}$) of dissolved residual chlorine containing species to
        measure the current flow (i_2) through the cell associated with the discharge, at
        the working electrode, of electrochemically dischargeable chlorine containing
        species,

(x)   measuring the pH (pH2) of the calibration water sample,

(y)   determining the fraction (f_2) of the total dissolved chlorine which is present as said electrochemically dischargeable species by the equation,

$$f_2 = \frac{1}{1 + \dfrac{10^{-x}}{y^{-pH2}}} \tag{15}$$

where x is 2.50 to 7.53 and y is 3.00 to 5.00,

(z)   using the values of i_2, f_2 and $Cl2_{tot}$ to determine a calibration factor (μ) for the cell representative of the amount of current per unit concentration of said electrochemically dischargeable species:

11.   A method as claimed in any one of claims 1 to 10 wherein the platinum working electrode is maintained at a potential of 250 mV relative to the reference electrode.

12.   A method as claimed in any one of claims 1 to 11 wherein the counter electrode is of platinum.

13.   A method as claimed in any one of claims 1 to 12 wherein the reference electrode is a silver/silver chloride electrode.

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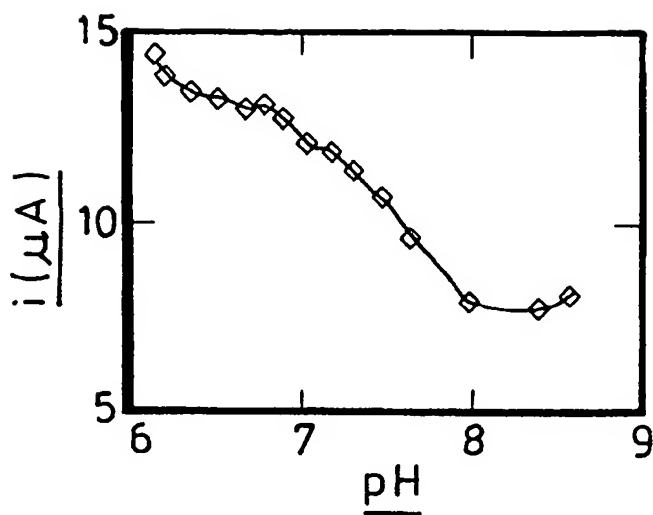
FIG.1
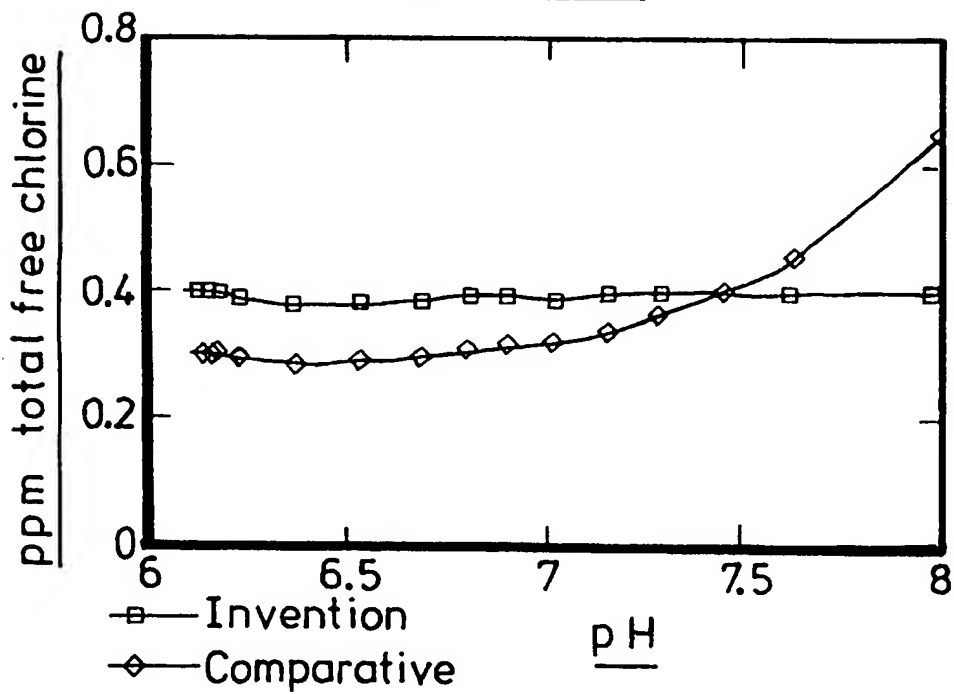
-□— Invention
-◇— Comparative

FIG.2

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G01N27/49

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 176 031 A (R. ROSENBLUM) 27 November 1979 see abstract	1
A	US 4 940 946 A (S. NAZARYAN) 10 July 1990 see abstract	1
A	US 5 230 785 A (P. A. YAGER) 27 July 1993 see abstract	1
A	WATER SUPPLY, vol. 13, no. 2, 1995, SOUTH AFRICA, pages 195-202, XP002035716 G. C. SOLYMOSI: "INTELLIGENT, MICROPROCESSOR-BASED AMPEROMETRIC ANALYSER ENABLES PART PER BILLION CHLORINE RESIDUAL MONITORING AND CONTROL" see abstract	1

☐ Further documents are listed in the continuation of box C.   ☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 July 1997	3 0. 07. 97
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Authorized officer Duchatellier, M

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4176031 A	27-11-79	JP 54130089 A	09-10-79
US 4940946 A	10-07-90	NONE	
US 5230785 A	27-07-93	NONE	